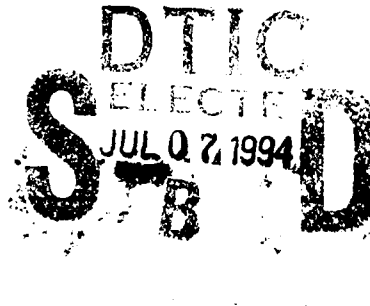FINAL   15 Mar 93 TO 14 Dec 93

CHEMISORPTION ENERGETICS OF SUPERREACTIVE CHLORINE
CONTAINING SPECIES ON GALLIUM ARSENIDE SURFACES

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Dr Andrew C. Kummel

Dept of Chemistry
Univ of California, San Diego
9500 Gilman Drive
La Jolla, CA 92093-0314

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Capt Thomas Erstfeld
AFOSR/NL
110 DUNCAN AVE SUITE B115
BOLLING AFB DC 20332-0001

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while those of F2 and O2 are quite distinct. For the heavy diatornic halogens (cl2,
Br2, and I2), the sticking probability increases with incident translation energies
above 0.1 eV, and the largest initial sticking probabilities are obtained at the
highest incident engergies, with S0 equal to 95 - 100% for I2 and Br2, at low
incident energies the initial sticking probability, S0, decreases with increasing
surface temperature while at high incident energies the sticking probability is
independent of surface temperature. In addition, for CI2 very low energy meolecular
beams can be prepared, and the sticking probability is observed to decrease with
increasing incident energies between 0.02 eV and 0.06 eV. Therefore, all these
heavy diatomic halogens can adsorb via precursor - mediated chemisorption at low
incident translation energy and via direct - activated chemisorption activated
chemisorption at high incident translational energy. For all incident kinetic
energies, the chemisorption probability decreases linearly with coverage (S=S0(1-0))
for the three diatomic halogen gases. This suggests that a single site is required
to initiate the direct chemisorption process and the precursor is intrinsic.

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Title: Chemisorption Energetics of Superactive Chlorine...
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Andrew C. Kummel, Dept. Chem, Univ. Cal., San Diego (UCSD)

(a) Cl_2, Br_2, I_2, and F_2, O_2 Chemisorption on Si(110) 2x1

The chemisorption mechanisms of Cl_2, Br_2, and I_2 on Si(100) 2x1 are quite similar while those of F_2 and O_2 are quite distinct. For the heavy diatomic halogens (Cl_2, Br_2, and I_2), the sticking probability increases with incident translation energies above 0.1 eV, and the largest initial sticking probabilities are obtained at the highest incident energies, with S_0 equal to 95 - 100% for I_2 and Br_2, and 80 - 85% for Cl_2. At low incident energies the initial sticking probability, S_0, decreases with increasing surface temperature while at high incident energies the sticking probability is independent of surface temperature. In addition, for Cl_2 very low energy molecular beams can be prepared, and the sticking probability is observed to decrease with increasing incident energies between 0.02 eV and 0.06 eV. Therefore, all three heavy diatomic halogens can adsorb via precursor - mediated chemisorption at low incident translation energy and via direct - activated chemisorption activated chemisorption at high incident translational energy. For all incident kinetic energies, the chemisorption probability decreases linearly with coverage ($S = S_0(1-\Theta)$) for the three diatomic halogen gases. This suggests that a single site is required to initiate the direct chemisorption process and that the precursor is intrinsic.

Currently, we are studying the chemisorption mechanism for F_2 and O_2 on both Si(100) 2x1 and Si(111) 7x7. Both F_2 and O_2 have chemisorption probabilities which increase with incident translational energy indicating that they have the usual activated chemisorption mechanism at high translational energy. In addition, they both exhibit the inverse temperature effect: at high translational energy, the sticking probability increases with increasing surface temperature. This has been seen before for O_2/Si(100) by Engel and was ascribed to thermally assisted activated chemisorption; however, our results on F_2/Si(100) & Si(111) show the mechanism is more intricate. For F_2/Si(100) and Si(111), the activation barrier is sufficiently small that we can increase the translational energy so high that the sticking probability at 300 K goes to 100% and thus the inverse temperature effect disappears; we are now repeating these experiment on O_2/Si(100) & Si(111). Therefore, either at high translation energy the molecules can directly dissociation without passing through the thermally assisted molecular chemisorption channel or that there is more than one activated molecular chemisorption channel. We have also recorded the temperature programmed desorption (TPD) spectra of SiF_2 and SiF_4 from F_2/Si(100) and F_2/Si(111) and observed that the maximum coverage and TPD peaks are a function of the incident F_2 translational energy (Note: This data is still preliminary and needs to be recheck because it was taken with an effusive doser). The dependence of the TPD and coverage upon incident energy is almost certainly due to F_2 adsorbing via abstraction at low incident energies. The abstraction mechanism was first identified theoretically by Carter and experimentally by Ceyer. Our results show that the chemisorption state of the F atoms from abstraction most closely resembles the chemisorption of F atoms from XeF_2 as opposed to thermal F or F_2; this would seem to indicate that some of the exothermicity of abstraction is channeled into the chemisorbing F atom.

(b) Cl_2/GaAs(100) Ga-c(8x2), GaAs(100) As-c(2x8), GaAs(110) 2x1

Initial sticking probabilities were measured for monoenergetic molecular chlorine upon the Ga-rich GaAs(100) c(8x2), As-rich GaAs(100) c(2x8), and stoichiometric GaAs(100) (1x1) surfaces. Our data indicate the presence of both precursor and direct activated chemisorption mechanisms on all three surfaces. The average barriers to direct chemisorption are quite similar on these three surfaces, suggesting both structural and elemental insensitivity for the direct component to chemisorption. Measurements of sticking versus coverage at low energy showed that the precursor mechanism is intrinsic at 300 K. Total energy scaling is observed on both the Ga-rich GaAs(100) c(8x2) surface and the stoichiometric GaAs(110) (1x1) surface for both precursor mediated and direct activated chemisorption, indicating highly corrugated gas - surface interaction potential.

GaAs(100) and GaAs(110) surfaces by Cl_2. The Ga-rich GaAs(100) Ga-c(8x2) and the stoichiometric GaAs(110) (1x1) surfaces form stable ordered monochloride overlayers when exposed to Cl_2 at 300 K. The ordered overlayers formed are AsCl on the GaAs(110) (1x1) surface and GaCl on the GaAs(100) Ga-c(8x2) surface. In contrast, the As-rich GaAs (100) As-c(2x8) surface undergoes continuous uptake of Cl_2 under equivalent conditions. All three surfaces exhibit continuous uptake of Cl_2 at surface temperatures above 600 K, where continuous etching is known to occur. We have shown that the Ga-rich GaAs(100) Ga-c(8x2) and the stoichiometric GaAs(110) (1x1) surfaces can be induced to undergo continuous etching at surface temperatures of 300 K, if they are first exposed to Cl_2 with surface temperatures above 600 K. This slight pre-etch disrupts the surface order and exposes multiple dangling bonds. The disrupted surface does not allow for a monochloride passivation layer to form; instead, volatile trichloride products form, leading to continuous etching. Therefore, the dissociative adsorption of molecular chlorine on GaAs(100) and GaAs(110) surfaces involves a competition between etching and passivation in which monochloride passivation is favored only on the well-ordered surfaces.

(c) STM of Local Adsorbate Structure as a Function of Chemisorption Mechanism

We have developed a unique machine to dose a crystal surface in ultra-high vacuum with a mono-energetic molecular beam and then examine the adsorbate structure with STM. Using this technique, we have identified the role of the chemisorption mechanism in formation of adsorbate structures for Cl_2, F_2, and O_2 upon Si(111)-7x7 surfaces at 300 K. When a Si(111)-7x7 is dosed with 0.05 eV Cl_2 (precursor mediated chemisorption), the dominant adsorbate structure is SiCl islands. The SiCl islands are hundreds of Angstroms apart at low coverage and nucleate at missing ad-atom defects. Conversely, for 0.44 eV Cl_2 dosing (direct activated chemisorption), island formation is not observed and only single site center-adatom preferred chemisorption is present. It is proposed that island formation results from Cl_2 adsorption via a mobile molecular physisorption state which dissociates at the edges of SiCl islands while center-adatom preferred reaction results from instantaneous direct-activated chemisorption.

For F_2 chemisorption on Si(111) 7x7, there is no intrinsic physisorption state physisorption state, and therefore no island formation is observed at low incident translational energy. Instead at low translation energy we observe that the dominant adsorption sites are single reacted adatoms while at high translation energy the dominant adsorption sites are pairs of adjacent center adatoms. At low translational energy, the F_2 adsorbs via abstraction whereby when a F_2 collides with the surface, one F atom chemisorbs while the other is ejected into the gas phase. Our STM results show that this abstraction mechanism accounts for nearly all the chemisorption at low energy because near all the adsorption sites are single reacted adatoms. At high translational energy F_2 adsorbs primarily by dissociative chemisorption, and thus we observe adjacent pairs of reacted adatoms. The dominant type of reacted silicon pair is center adatoms from adjacent unit cells; this is due to the center adatoms being more reactive as well as center atoms from adjacent unit cells being more weakly electronically coupled than center adatoms in the same unit cell.

For O_2 chemisorption on Si(111) 7x7 and Si(100) 2x1, there is precursor mediated chemisorption at low incident energies and directly activated chemisorption at high incident translational energies, but there precursor mechanism is very weak ($S_0 < 5\%$). Previous STM by several group had shown that there were two types of sites: insertion of oxygen atom into the adatom-rest atom bond ("bright sites") and bonding of oxygen atoms onto the adatoms dangling bond ("dark sites"). We measured the local structure with STM both with low incident energy O_2 (precursor mediated chemisorption) and at high incident energy O_2 (direct activated chemisorption). We observed that the ratio of bright to dark sites is invariant with translational energy which shows that sites selectivity is based upon the impact parameter. We also observed that the ratio of Si-O- bright site corner adatoms to center Si-O- bright site adatoms changes with incident O_2 translation energy: 2:1 ratio at high translational energy (direct activated channel) and 1:1 ratio at low incident translational energy (precursor mediated channel). This is consistent with the notion that the structure of the activation barrier differs for molecules incident from the gas phase versus from the physisorption state. The preference for corner Si-O- adatoms for direct activated chemisorption indicates that the activation barrier from the gas phase is lower for the adatom with the greatest dangling bond character. the corner adatom: this is very reasonable since for O_2/Si(111) 7x7 chemisorption probably involves the formation of an O_2^- state via a harpooning mechanism.

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